OAR Box 1824

Prepped by Charmelle Mathews

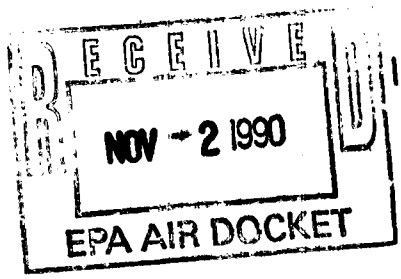
Document Number:

(154) IV-D-203

Docket Number:

A-90-16

A-90-16
IV-D-203



Environmental and Safety
Engineering Staff
Ford Motor Company

The American Road
Dearborn, Michigan 48121

October 29, 1990

Air Docket (LE-131)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Attention: Docket No. A-90-16

The information provided with this communication reflects Ford Motor Company's comments on the submission provided by Ethyl on August 10, 1990. That submission contained comments by Ethyl Corporation in response to the automotive industry on the waiver request for HiTEC 3000, as published in the June 5, 1990 Federal Register Notice.

The August 10, 1990 Ethyl submission attempted to discredit the automotive industry statements regarding the adverse effects of MMT on vehicles emissions and emission control components. Ethyl stated that the industry comments were inadequate to prove MMT will have an adverse effect on vehicle emissions and emission control components and that false information was provided to support these claims. Therefore, Ford submits the attached comments and data in order to clarify and correct the issues raised by Ethyl Corporation.

Our comments include:

- Clarification of the applicability of data from Canadian vehicles:
  - The concentration of MMT in Canadian Fuel typically is only 21% to 42% higher than the MMT concentration requested in the current waiver application.
  - Despite more extensive U.S. inspection and maintenance programs, catalyst warranty return rates in Canada are greater; together with the catalyst inspections and analyses submitted previously, this implies that MMT may be a major contributor to this increase.
- Discussion of Ford's concern regarding Ethyl's test procedure and statistical analyses.
- Further explanation of the catalyst studies performed by Ford which, in Ethyl's response, were stated to be lacking.

Ford continues to believe further testing must be performed to determine whether MMT will adversely affect vehicle emissions or emission control components before a determination can be made of the ability of HiTEC 3000 to meet the criteria for a grant of this waiver.

Sincerely,

David L. Kulp
Manager, Fuel Economy
Planning & Compliance

Enclosures

FORD MOTOR COMPANY'S REPLY COMMENTS TO ETHYL CORPORATION'S AUGUST 10, 1990 SUBMISSION TO EPA REGARDING THEIR APPLICATION FOR WAIVER TO ALLOW THE ADDITION OF MMT TO UNLEADED GASOLINE

On August 10, 1990, Ethyl Corporation ("Ethyl") provided to EPA a rebuttal to comments submitted by the automotive industry, including those provided by Ford Motor Company ("Ford"), during the open comment period ending July 23, 1990. Ethyl's response attempted to discredit the statements regarding the adverse effects of MMT on vehicle emissions and emission control components by leading the reader to two conclusions. First, that the auto industry comments were inadequate to prove MMT will adversely effect vehicle emissions and emission control components and second, that false information was provided in support of Ford and other auto industry claims. In fact, the opposite was true. To those unfamiliar with the chemical and technical issues, Ethyl's submission may appear to offer counterpoints to several issues raised by Ford, but upon closer examination it is apparent that Ethyl has not used valid scientific techniques in gathering and analyzing the necessary data. Ethyl's superficial presentation paints a rosy picture of MMT, but it does so with misleading, incomplete information and misrepresentation. Accordingly, Ford submits the following comments in order to clarify and correct these issues.

MMT, AT 1/32 GRAM MN/GALLON, WILL CAUSE ADVERSE EFFECTS ON EMISSIONS AND EMISSION CONTROL COMPONENTS

Ethyl maintains that "[i]f use of the Additive plugs catalysts, as the auto companies claim, they could have provided detailed information regarding differences in catalyst-warranty claims in the U.S....and Canada..." (pp. 18-19). Furthermore, Ethyl contends that data from Canadian vehicles cannot be considered since the allowed concentration in Canada is twice as high as that proposed in the application. The following discussion demonstrates that not only does our data from Canadian cars show that MMT at the concentrations allowed in Canada cause significant adverse effects to vehicles emission control components, but also that the concentrations used in Canada are much lower than the allowed 1/16 gram/gallon. Therefore, the failures observed in Canada are likely to occur in the U.S. at the proposed MMT concentration.

- **Rates of Catalyst Returns Under Warranty Are Substantially Higher in Canada than in the U.S.**

  We have recently completed an investigation of projected warranty return rates for 1989 model year vehicles for both Canada and the U.S. which shows that on average, Canadian cars have a 75 percent higher rate of catalyst warranty returns than American cars. These numbers are confirmed by the volumes of actual warranty returns which show that the weekly rate of catalyst warranty returns is approximately twice as high in Canada as it is in the U.S. These discrepancies come despite U.S. inspection/maintenance programs, unparalleled in Canada, that test nearly 40 percent of the U.S. passenger car fleet for failures of emission control components. We would expect that if Canada implemented a similar program, their rates of warranty returns would increase, creating a larger disparity between the two rates. Although we recognize that there are other factors which may have contributed to this higher rate of return, previous studies indicate that the failures may be the result of MMT in Canadian fuel -- our July 23 submission to

EPA provides an in-depth analysis of 41 catalysts removed from Canadian vehicles. This analysis showed that manganese oxide deposits on the catalysts greatly reduced catalyst conversion efficiency. Plugging was also proven to be a significant concern. Because these catalysts had been selected at random from catalysts returned under warranty, they provide an unbiased representation of catalyst failures in Canada. Therefore, we can conclude that MMT has significant adverse effects of vehicle catalysts, as detailed below.

Despite these failures in Canadian catalysts, Ethyl claims that plugging of the catalysts has no basis in fact. They claim the additive does not cause plugging of the catalysts (page 16). In Ford's written comments, photographs of the front face of catalysts clearly show that the catalysts were indeed plugged or coated with a heavy layer of Mn_3O_4. It should be noted that it is not necessary to completely plug the channels to cause deactivation of the catalyst. Catalyst deactivation can result at even low Mn concentrations as shown in Ford's data by a residual layer over the washcoat that prevents or delays the interaction of the exhaust gases with the active catalytic agents (mass transfer resistance). Ethyl's discussion of these photographs repeated their previous arguments that data from Canada cannot be considered due to the higher allowed concentration allowed there. However, as we will discuss below, the actual MMT concentrations seen by Canadian vehicles are much lower than the allowed 1/16 gram/gallon MMT. While post-mortem analyses on the catalysts from the Ethyl test fleet ascertain whether plugging will occur through the use of MMT at 1/32 gram/gallon, under certain conditions, Ethyl has failed to perform these analyses. (See also Attachment 1, #2-Responses to Ethyl's Attachment 5.)

In our July 23, 1990 submission, we included a table of engine-out data (Ford July 23, 1990 submission, Attachment 5, Table 2) for the Ethyl test fleet. Ethyl took exception to this table in their rebuttal, stating that these engine-out values were "inconsistent with the data in ETHYL4S2" and were unreproducible (Ethyl Comments, Attachment 3). These values came directly from the engine-out data presented by Ethyl in both earlier information provided to Ford and in their waiver application. These values were also used in the calculations of catalyst efficiency which were submitted to the docket.

From Ethyl's Attachment 3, it appears that the engine-out values that we had analyzed, and were used by Ethyl to calculate catalyst efficiency, were the average of the first two engine-out measurements (prior to maintenance) at each mileage interval. However, the entire data set (before and after maintenance) was used to determine the effect of MMT on engine-out emissions. This inconsistency is highly questionable and suspicious. If the average of the first two engine-out measurements represented engine-out characteristics sufficiently for catalyst efficiency determination, then they should also have been used for the determination of the effects of MMT on the engine-out emissions. Our table of these engine-out emission values showed that MMT caused engine-out emissions of HC to increase and NOx to decrease. Although we concede that the amount of variability in Ethyl's data precludes a definite conclusion that this is the effect of MMT, the data does indicate a trend which is a cause for significant concern. (See also Attachment 1, #3.)

As a final endeavor to prove that MMT does not adversely effect catalyst conversion efficiency of HC and CO (and beneficial NO_x reduction), Ethyl prepared an analysis to determine the statistical relationships between the key elements reported by Ford -- namely conversion efficiency, BET, surface area, precious metal loading and the composition of the coating on the catalyst (pages 26-27) (see Attachment 1, #1). We believe that it can be demonstrated that this analysis was flawed from the concept. Ethyl used only the point of stoichiometry, R=1, to make its regression analysis. However, best overall catalyst function occurs at the 1.0 value and vehicles normally operate within a range of R=0.8 to 1.8. Ethyl further compounds its mistake by indicating that barium and cerium are contaminants. Barium and cerium are integral components of the catalyst. Ethyl contends that lead and zinc in the Ford post-mortem analysis are the true culprits behind the loss in efficiency, rather than Mn_3O_4. However, data presented at SAE in response to this claim show that, at the concentration levels of lead, phosphorous and zinc seen on the Canadian catalysts, lead and zinc were not major contributors to catalyst deterioration. (See also Attachment 1).

We have informed Ethyl on several occasions that post-mortem analyses on their catalysts, if performed correctly, would provide more definitive evidence that MMT has no adverse effect on the catalysts, at least under the conditions simulated. This is based on years of experience, not only at Ford but at all the automotive and catalyst manufacturers, which have shown that the best way to test a catalyst is to combine comprehensive laboratory tests with vehicle emission and durability tests and, most importantly, a complete post-mortem analysis. These analyses are standard, well-characterized laboratory tests which have been developed over a number of years and are preferred over vehicle tests in many instances because of their greater reproducibility and reliability. Ethyl claims that the results of these analyses are invalid because they are conducted under "simulated laboratory conditions and do not test under real world conditions" (page 24). This argument is erroneous. We do not simulate laboratory conditions, we simulate vehicle conditions. The gases that are flowed over the catalysts are simulated auto exhaust gases, a mixture of propane, propylene, carbon monoxide, nitric oxide, sulfur dioxide, nitrogen and oxygen. The catalyst sees the same gases during vehicle operation.

Not only has Ethyl failed to perform any of these post-mortem tests but, in fact, has claimed in the rebuttal that the procedures for these tests are proprietary to Ford, thus excusing them from not conducting the tests. In light of our numerous offers of assistance in this area (see Attachment 3), Ethyl's claim is without foundation. Ethyl, or any catalyst supplier, is fully capable of performing the studies that could end all conjecture about the effect of MMT on the program's emission control components.

- **Data From Canadian Vehicles are Applicable to this Waiver Application**

Ethyl has argued against the significance of data from Canadian vehicles due to the MMT concentrations allowed in Canada being twice as high as that proposed in the recent waiver application. However, fuel surveys show (data concurred by both Shell Canada, Esso Canada and

Ethyl Petroleum-Toronto) that the actual MMT concentrations in Canadian fuel average between 0.03785 and 0.04542 grams/gallon. These concentrations are only 21-42 percent higher than the MMT concentrations requested in the current waiver application. In addition, some of the catalysts which we had analyzed and discussed in our previous submission came from Canadian vehicles with low mileage. Yet the manganese oxide deposits in the catalyst were visually and microscopically evident as a distinct layer over the washcoat. Using this data, one can extrapolate that even with a lower concentration of MMT in the fuel, at the higher vehicle mileages, the same heavy coating and possible plugging of the channels would result. Therefore, it appears highly likely that, should this waiver be approved, we will soon experience the same types of Mn_3O_4-related problems on U.S. emission control systems that we are currently experiencing in Canada.

- **MMT Will Increase Hydrocarbon Emissions**

Ethyl contends that the dissenting automotive commentors did not review the fleet data and, in failing to do so, subsequently failed to address the validity of Ethyl's voluminous data base (page 8). In Ford's case, this is simply not true. Our analysis of Ethyl's data resulted in several of the concerns discussed in our earlier submission. Ethyl's data clearly show that HC emissions increase by a relatively large percentage during their purported "real world" testing. In view of the future, stringent emission standards contained in the pending Clean Air Act, any increase in HC emissions must be viewed as a potential problem. This increase in HC emissions may have been the impetus that led the California Air Resources Board (CARB) to rule, on September 28, 1990, that manganese and manganese-containing additives cannot be added to state gasolines.

As stated in Ford's response, Ethyl's data, as well as previous studies on MMT (such as SAE 790706, "Results of Coordinating Research Council MMT Field Test Program", 1979), have given us strong reason to believe that MMT increases HC and decreases NO_x in the engine-out emissions. Although Ethyl objects to this claim, they have failed to provide adequate data which demonstrate that MMT has no effect on engine-out emissions. As discussed above, the engine-out data provided by Ethyl to the docket may not be representative of the actual feed-gas composition.

Furthermore, Ford's extensive experience and technical understanding of engine deposits and the effects on emissions leads to the conclusion that MMT will increase engine-out hydrocarbons. The primary source of engine-out HC is due to crevices in the combustion chamber that accept HC vapor, but are too small to support flame propagation. Hence, the HCs escape combustion and are released from the crevice during the expansion stroke and then exhausted. A deposit layer, such as manganese oxide, can increase HC substantially over a clean engine. The deposit builds up fairly quickly with mileage, then tends to stabilize, since newly formed particles do not stick as well to the particles as they do to cooler, metal surfaces of "green" (new) engines. Ethyl's claim that Mn_3O_4 deposits do not form in the combustion chamber is based on their inability to retrieve any such deposits. However, scavenging deposits out of combustion chambers is a difficult task. Ethyl used very aggressive scavengers (ethylene

dibromide and dichloride) to help control lead accumulation, but these are too toxic for use today. We do not know of any successful attempt to scavenge manganese oxide.

- **There Is No Evidence that MMT Will Not Effect Compliance to Future Standards**

Ethyl claims to have proven that MMT will not affect vehicle compliance with future emission standards through "...an analysis based on actual test data rather than pure speculation" (page 15). However, the analysis performed by Ethyl to prove that MMT would not effect vehicle compliance to future HC standards contains numerous assumptions. First, none of the 1988 models upon which Ethyl bases its analysis have emission control systems designed for future emission standards -- systems which provide for fast light-off and yield lower feedgas levels. Thus, the program certainly does not provide "actual test data". Second, all the analyses are based on regressions. Regressions provide theoretical responses, not "actual test data." Therefore, it is impossible for Ethyl to have concluded, definitely, that MMT will not affect compliance to future standards.

- **Apparent Reductions in NOx Emissions Are also Cause for Concern**

In its August 10 rebuttal, Ethyl also noted that "Ford asserts that '[t]here appears to be no definitive explanation for the NO_x reduction' in the test program. The two independent statistical experts who analyzed the test program data, however, attribute the reduction in NO_x emissions to the use of the Additive" (page 36). This statement misrepresents Ford's comments and completely misses the point. The discussion included in our July 23 comments agreed with Ethyl's conclusion that their test data indicated that MMT reduced NO_x emissions. However, reduced NO_x emissions in the engine-out gases are a source of concern and create two important issues. First, the decrease in NO_x suggests that the engine is not operating correctly. The second concern is that an increase in HC emissions generally accompanies decreases in NO_x emissions. Any additive that increases HC emissions creates a serious concern.

In the July 23 submission, Ford presented several possible explanations for the apparent MMT effect on HC and NO_x engine-out emissions. Ethyl attempted to discredit these by stating that the theories were "inconsistent with Ford's own assessment of the engine-out data. For example, at 50,000 miles the engine-out NO_x emissions are listed as higher for the Ford Escort using fuel containing the additive" (page 37). This statement is absurd. The data show that for the four measurements of engine-out taken from the Escort and Taurus, at 50k and 75k miles, the Escort at 50k miles is the only data point which shows a higher NO_x for the MMT vehicles. The GM data, provided in their submission, confirms that MMT appears to increase engine-out NO_x by showing that out of four cars at 50k, NO_x engine-out emissions are higher by an average of 0.10 gram/mile for the cars fueled with gasoline containing MMT.

Ethyl contends that the manganese oxide deposits that coat the vehicle exhaust system are responsible for the apparent NOx reduction. They support this conclusion by citing SAE 821193, written by Williamson, et al, (Attachment 2, page 5) which states that manganese oxide may catalytically reduce oxides of nitrogen. However, this same paper goes on to say, "This mechanism would be effective as long as catalyst retention of Mn_3O_4 is not so excessive as to result in mass transfer limitation on the catalyst." However, our physical and chemical characterizations show clearly and conclusively that Mn_3O_4 is retained excessively on the catalyst, creating a layer as much as 81 microns thick. This retention results in mass transfer limitations contributing to the increased HC emissions. In addition, Williamson's, et al, concluding remarks include the following statement: "Lower levels of Mn would also decrease the well documented possible effects of Mn_3O_4 deposits which may plug catalysts and oxygen sensors, as well as increase combustion chamber deposits giving rise to higher HC feedgas levels." This is exactly what Ethyl's "real world" data show.

Ethyl further states that their "waiver request included a report from Dr. Roy Harrison which stated that the reaction temperatures and residence times in automobile exhaust systems were of the right order of magnitude to convert NO_x. This information, together with patent information (3) Japanese patents that claim Mn as a catalytic agent), clearly shows that the catalytic properties of Mn_3O_4 plausibly explains the reduction in NO_x emissions observed in Ethyl's test program" (Attachment 2, page 11). First of all, Dr. Harrison's objective was to determine if the catalytic activity of Mn_3O_4 was of potential interest in air pollution control and, in addition, to provide information on the effects of MMT. His experiments were run in a flow reactor with purified air. Harrison states that the results demonstrate that Mn_3O_4 can accelerate the decomposition of NO in purified air at moderate temperatures. He does not relate any of his experiments to automotive exhaust or even simulated automotive exhaust. However, Harrison does makes the statement that it may explain the effects of MMT under automotive exhaust conditions based on purified air, not engine exhaust components. On the other hand, Ford believes that this decomposition is not feasible under automotive exhaust conditions and that NO removal requires reduction, not decomposition (Ford's original submission to the EPA). Moreover, there is no contention by Ford that Mn_3O_4 will not act as a catalytic agent, but that it will not under automotive exhaust conditions be an effective catalytic agent. Furthermore, automotive exhaust contains potential catalyst poisons, such as sulfur, lead, and phosphorus, not present in purified air. Williamson's, et al, state in their paper that Mn_3O_4 acts as a scavenger for these contaminating species and, as such, become poisoned very quickly in the exhaust stream. This is the fundamental difference between an experiment run with purified air and one run with simulated engine exhaust gases. As a further explanation, Figures 6 and 7 (Attachment 1) show that in the rich Air/Fuel region as the concentration of manganese increases the level of NO_x conversion decreases; similarly, the selectivity to NH_3 increases.

Finally, Ethyl has made reference to the three Japanese patents that were issued regarding NO_x reduction by Mn_3O_4 as support for their theories. However, it should be noted that many patents are issued, but not all of them are considered useful. The Japanese auto companies do not make use of these patents for their own catalysts. In fact,

they oppose the addition of MMT to U.S. gasoline (see submission of AIAM to EPA). Furthermore, if Mn_3O_4 provided such great NO_x reduction, then it would certainly provide an inexpensive source of rhodium replacement in catalysts and would already be in widespread use.

FORD'S CONCERNS REGARDING ETHYL'S TEST PROCEDURES AND ANALYSIS

Ethyl emphasized throughout its rebuttal that Ford did not acknowledge the statistical analyses. Ethyl concluded that this omission demonstrated that Ford was "[u]nable to rebut the core of Ethyl's case..." (page 9). However, it was obvious in Ford's earlier submission that we suspect the validity of Ethyl's fleet data. As stated in our July 23 comments, we do not believe that Ethyl conducted their testing program accurately. Therefore, since we did not believe that the raw data was accurate, we saw no reason to discuss the subsequent analysis of this incorrect data.

Nevertheless, Ford is providing comment on the validity of the statistical data herewith. However, even the best analysis, if performed on inappropriate data, will yield poor results. Our criticism of the fleet data is based primarily on two issues: the design of the test program which created tremendous variability in the data, and the baseline from which Ethyl made its comparisons, to determine the relative effect of MMT on vehicle emissions, which was incorrect.

- **The High Variability in Ethyl's Fleet Data Precludes Meaningful Analysis**

  Based on the highly variable data provided by Ethyl (graphs of Ethyl's data showing high variability are included in Attachment 2), it would be impossible to statistically conclude that there is a difference between emissions from vehicles operated on clear fuel and those operated on clear fuel with MMT. The high data variability attests to the poor design and execution of Ethyl's test procedures. (See also Attachment 1, #4).

  Although Ethyl attempted to give the impression that it did everything possible to eliminate variability in the test procedures, an in-depth analysis of their techniques shows quite the opposite. The most significant errors were realized in the procedures for emission data acquisition. For no apparent statistically supported reason, the data from the first two vehicle emission tests were evaluated and compared. If it was determined that one of these points was inaccurate and should be discarded, a third test was performed. If procedural error was not involved, the scientific validity of this practice is questionable. Although this methodology lends the outward appearance of credibility to the argument that Ethyl did as much as possible to reduce test variability, it raises the point that Ethyl failed to design and carry out an experiment that would detect specific size differences in the emission values if they existed. These techniques are well known and can be found in any good statistics/math text. The Ethyl experiment was flawed. Failure to set a goal on sample sizing practically guaranteed that no significant difference between fuel with MMT and without would be detected.

Ethyl has critical omissions in their test procedures which cause additional suspicions regarding the reliability of their data and subsequent conclusions. Ethyl also failed to provide evidence of emission laboratory correlation between the two test sites. Although the labs did cross-reference emission results via blind testing of standard reference gases, the vehicle emission testing itself was not correlated. Emission testing has many sources of variability, including dynamometers, drivers, ambients, etc. Commonization of results from site-to-site and vehicle fleet-to-fleet are probably precluded because the overall sites have not been correlated. Furthermore, Ethyl did not keep records of oil consumption for the test cars. These records provided valuable information regarding vehicle performance and are necessary to perform a complete evaluation of the effects of MMT. Also, for no apparent reason, Ethyl replaced the fuel injectors on all the vehicles at 50k miles. Ethyl has claimed that based on lack of driveability problems, the fuel injectors did not become fouled in the vehicles operating on either clear fuel or with fuel containing MMT. However, the replacement of the fuel injectors, which is not part of routine maintenance, precludes this conclusion and casts suspicion over the validity of the emission data after 50k miles.

The following provide response to the other specific issues raised in Ethyl's rebuttal.

Finally, the presentation of the results of the statistical analysis on the effects of MMT as point values was misleading. Point values do not provide confidence intervals which provide an indication of the precision of the values. Due to the variability throughout the Ethyl data, we would expect that such confidence intervals would be large and mask even significant differences between the MMT and baseline vehicle performances.

- <u>The Baseline Used for Comparative Analysis Was Inappropriate</u>

We maintain our earlier position that the baseline used to determine the comparative effect of MMT was inappropriate. In their defense for the use of this fuel, Ethyl stated that Howell EEE meets "rigid specifications" and contains very low concentrations of olefins. Also, they claimed that due to its "inherent stability, an additive package is unnecessary to protect from fuel deposits formulation." These statements are essentially meaningless. First, the mere fact that the fuel meets specifications on some chemical analyses does not mean that the specifications cover the important matter of detergency, our major objection. Furthermore, we have no technical assessment as to the impact of olefins other than it is "suspected" to contribute to deposit formation. Finally, "inherent stability" relates to oxidation and <u>not</u> to deposit formation due to combustion. These statements may, intentionally or unintentionally, mislead the non-technical reader into believing that Howell EEE, in view of these "specifications" could not lead to deposit buildup.

Despite ample opportunity, Ethyl has not provided sufficient evidence to prove that no deposit formation occurred in the baseline vehicles. Fuel injector flow data, physical examination of combustion chambers, and post-mortem catalyst analyses may have provided irrefutable proof

of their claims. But Ethyl has made no attempt to provide any of this information to substantiate their conjecture that the baseline vehicle emissions were not affected by deposit formation.

Ethyl supports their decision to perform the mileage accumulation on clean fuel to reduce variability due to additives that may complicate their analysis of the effects of MMT. However, this attempt to reduce variability has actually increased it substantially by adding the unknown variable of vehicle performance on clear gasoline to their conclusions. Fuel additives are necessary to provide an analysis which is applicable to the real world. Vehicles operated on fuel without additives cannot be expected to behave like vehicles operated on fuel with additives. Ethyl compared emissions from cars running on clear fuel with MMT and without MMT and applied these results to conclude that MMT will have minimal effects on vehicles operating on commercially available gasoline. Moreover, they cannot draw this conclusion without knowing how the performance of cars on clear fuel correlates with that of cars running on commercially available gasoline. The additional testing which Ford requested will provide this correlation so that the effect of MMT on vehicles operating on commercial gasoline can be determined. Despite Ethyl's attempt to avoid adding variables to their calculations, that is exactly what they have done.

Ethyl has claimed that auto companies and EPA were aware of their choice to use Howell EEE fuel for mileage accumulation from the beginning (pages 3-4). While Ethyl may have always intended to use Howell EEE clear fuel for mileage accumulation, that intention was never made clear to others. We were not made aware of Ethyl's intention to use Howell EEE clear fuel for mileage accumulation until approximately 30k miles had already been run. Standard, EPA approved procedures use indolene only for emission tests -- mileage accumulation is run using a fuel representative of commercially available gasoline. Furthermore, Ethyl's letter to EPA (provided in Appendix 1 of their submission) states that emission tests will be performed using Howell EEE, but there is no mention that this fuel would also be used for mileage accumulation.

FURTHER TESTING ON MMT MUST BE CONDUCTED BEFORE THIS WAIVER APPLICATION CAN BE APPROVED

Ethyl has claimed adamantly that no further testing is required to gain the approval of their waiver request. They have stated that "[t]he request for 'more testing' should be recognized for what it reflects -- an inability to refute the merits of Ethyl's application and, unlike a meaningful discussion and analysis of Ethyl's data, does not demand rigorous analysis" (page iii). We believe that both our July 23 submission and the above comments represent the results of "rigorous analysis" of Ethyl's data which proves that there is reason to believe that MMT will adversely effect vehicle emission control systems. We acknowledge that Ethyl has already invested substantial time and money in their test program. However, the additional testing which we require is not nearly as intensive and could provide the information needed to conclusively determine the effects of MMT on emission control components. We are disappointed by Ethyl's reluctance to perform these analyses.

Other industry comments support our position requiring further testing. Although Ethyl misrepresented the comments from General Motors to conclude that MMT should be approved ("General Motors -- the largest automobile manufacturer in the world -- does not challenge that Ethyl has satisfied the legal standard for approval of its waiver application") (page ii), the recommendation actually made by GM was that "EPA consider a conditional approval of the Ethyl waiver request and also that Ethyl conduct tests to provide additional data on the potential problems its additive could present for light-duty trucks and vehicles designed to meet more stringent exhaust emissions standards." It is interesting to note further that GM of Canada is very much opposed to the use of MMT in gasoline. The following recommendation was made in a letter sent from GM Canada to Environment Canada/Transport Canada (dated October 3, 1989): "We strongly support the activities...to reduce the amount and reactivity of emissions and reduce air toxics. In Canada, we encourage...elimination of MMT."

ADDITIONAL COMMENTS REGARDING THE ETHYL SUBMISSION WHICH WERE NOT DISCUSSED ABOVE

- **"The culmination of this program will provide an extensive database on the performance of current technology automobile gasoline engines using unleaded gasoline containing MMT Antiknock Compound. It is our goal to demonstrate that the use of MMT in unleaded gasoline will not cause or contribute to failure of any emission control devices or systems over the useful life of vehicles in which such devices or systems are used to achieve compliance with the Clean Air Act, Section 206 emission standards. (Attachment 1, Page 3)**

  The goal should have been "to determine whether the use of MMT would cause..." This is a seriously biased attitude that probably affected how the entire test was handled. The word "demonstrate" connotes knowing the final answer before commencing the fleet testing.

  This was, in fact, never demonstrated. Important emission control devices were not thoroughly evaluated for degradation during the test. With a topic as important as MMT, one should not have waited for failure; interim information was critical, and never collected. For example, it is amazing that oil consumption, another critical factor, was not recorded in any way.

- With regard to the health issue, "Moreover, automotive materials typically contain a large amount of manganese in their own right, averaging 7 to 8 pounds of manganese in the form of steel alloy. Given this amount of manganese in cars, one can reasonably question the depth of the automobile companies concern about manganese" (page 20, footnote #53). Does Ethyl actually mean that tiny airborne Mn_3O_4 particles formed by the combustion of MMT can somehow be related to the amount of Mn in steel alloys used in the manufacture of cars? This is an absurd comparison which leads us to question the credibility and relevance of other comments made by Ethyl.

- Ethyl claims that, "Recognizing that the catalyst has been exposed to such abnormal conditions is extremely important, as noted by the comments filed by Imperial Oil of Canada" (pages 26-27). They

reference the overtemperature conditions experienced by some of the catalysts examined in the first two series of analysis conducted by Ford. Imperial Oil of Canada is incorrect, in their statement that engine exhaust temperatures can get high enough to melt a catalyst substrate. Poor combustion in the engine can cause unburned fuel to burn on the catalyst, thus resulting in temperatures greater than the melting point of cordierite (T=2200°F). Moreover, they are also incorrect in their conclusion that plugging can only occur due to an out-of-tune engine. As noted above, Mn_3O_4 forms as a product of combustion and it coats the combustion chamber, the catalyst, the oxygen sensors, and fuel injectors (deposits result in misfire). Based on data from the Canadian catalysts, calculations show that approximately 25% of the combustion product of MMT, Mn_3O_4, is retained on the catalyst. (It might also be a prudent suggestion for Imperial Oil to examine a few catalysts from Canada.)

- "Another item which should be addressed relative to Ford is the difference between pre-1988 Canadian standards and current U.S. Standards. Of the 52 Canadian catalysts reported by Ford, only 11 were from 1988 or newer model year vehicles. Conversion efficiency information from the remaining catalyst cannot be compared to a U.S. catalyst. Those Canadian catalysts were designed for different standards" (Attachment 2, page 4). According to this statement, Ethyl implies that Ford designs its catalysts one way for the U.S. market and another way for Canada. Of the total of 31 cars used in the Ford analysis, six cars were from 1984, six from 1985, four from 1986, seven from 1987, seven for 1988, and one from 1989. The majority (>90%) of the vehicles examined in these studies had catalysts that were designed for 49-states and Canada. In other words, there were no differences in those catalysts supplied for Canadian vehicles. In those cases that were specific to Canada, only the precious metal loadings were different. In this instance, one would not expect to see a significant difference in emissions. Furthermore, Ford's comparisons of vehicles with and without MMT were made on the same model-year basis in order to assure there would be no difference between catalysts. Ethyl is simply not correct in its claim that Ford's catalysts are designed differently for Canada.

Ethyl's rebuttal also included several misrepresentations of previous Ford comments. The two most significant of those misstatements are corrected below.

- Ethyl stated in their rebuttal that "Ford claims that vehicle emissions improved after maintenance adjustments to the vehicle engines, and, therefore, that these improvements are not attributable to use of the Additive" (page 36). Ford never made this claim. Our comment that "[t]hese transitions at high mileage often tend to coincide with completion of repairs, routine maintenance, or possibly other systematic problems and should be analyzed further" was meant merely to suggest that further analysis may be needed to determine the relationship between the effects of MMT on emissions and other variables, such as repairs and maintenance.

- Ethyl claims that "Ford urges EPA to focus on individual models in its review of the Ethyl statistical analysis..." (page 34). Again, Ford never made any such statement. We did, however, express concern that by averaging the effects of MMT over the entire vehicle fleet, the performance of a few vehicles can effect the overall conclusion.

We agree with Ethyl's argument that they must only prove emission effects on the overall car fleet. However, Ethyl's test fleet, by excluding trucks and vans which represent nearly one-third of the U.S. vehicle fleet, fails to meet this requirement. Ethyl claims that trucks have similar configurations and, therefore, did not need to be included in the fleet. This is not a valid conclusion. The operating temperatures and loads of trucks are significantly higher than for cars. MMT would have a different effect on them.

In a further attempt to discredit the Ford comments, Ethyl exploited the errors made in the Ford July 23, 1990 submission. An example is Ethyl's lengthy discussion of the "errors" in Attachment 5, Figures 4 through 6, which were included in this submission. If Ethyl's analysis had been as thorough as they claim, they would have recognized that these figures represented not a gross mishandling of their data, as they infer, but rather a simple mislabeling error. The curves labeled as "Model C" were actually representative of "Model G" data, which were also included in the attachment.

ATTACHMENT 1

**FORD MOTOR COMPANY'S REPLY COMMENTS TO
ETHYL CORPORATION'S AUGUST 10, 1990 SUBMISSION TO EPA
REGARDING THEIR APPLICATION FOR WAIVER TO ALLOW
THE ADDITION OF MMT TO UNLEADED GASOLINE**

(1) "Ethyl determined the statistical relationships between the key elements reported by Ford -- namely, conversion efficiency, BET surface area, precious metal loading, and composition of the coating on the catalysts. This analysis shows that the presence of manganese on the catalyst reviewed by Ford did not affect conversion efficiency and, in fact, improved conversion efficiency for HC and CO emissions. Ford erroneously attributes the reductions in catalyst performance to manganese oxide (the most visible coating element) rather than the true culprits -- lead, zinc, and barium" (pages 26-27). Ethyl uses only the point of stoichiometry, R=1, to make its regression analysis, this is an incorrect assumption, in that the curves represented by R-value (redox ratio) are representative of a full range of Air/Fuel (A/F) ratio that is normally seen in vehicle operation. When this assumption is made, then Ethyl's conclusions are in error and may lead to gross misinterpretations of the regression results. The values of 0.8 to 1.8 are representative of a shift of approximately 3% in A/F. These shifts are normally seen in vehicle operation and consequently the range of redox ratios used in the laboratory analysis of the catalyst sweep this range of A/F. Ethyl further compounds their erroneous interpretation by indicating that barium and cerium are contaminants. Barium and cerium are integral components of the catalyst, they are not engine exhaust contaminates. Ethyl also contends that lead and zinc are the true culprits rather than Mn_3O_4. Data presented at SAE in response to this claim show that at the concentration levels of lead, phosphorus, and zinc seen on the Canadian catalysts they were not a major contributor to the deterioration of the catalyst. Figures 1, 2, and 3 show catalyst activity curves from separate vehicles. In these figures two vehicles have been run without MMT and one has been run with MMT. The lead, zinc, and phosphorus levels are higher or equivalent to the MMT fueled vehicle and yet the MMT fueled vehicle efficiency is lower. At the contamination levels seen in Ford's analysis they were not a problem as shown in the figures. If they were, they would have been excluded from the analysis and indicated as such. Those catalysts that were thermally deactivated or showed evidence of thermal deactivation were also excluded from the final interpretation of the effects of Mn_3O_4.

Furthermore, when a design matrix is not orthogonal, as in the Ethyl test fleet, the effects are confounded. In the case of fractional factorials, care has to be exercised in the interpretation of output from such regression analysis. In Ethyl's case, for example, a social science type data approach is utilized where no design matrix exists, thus, a non-orthogonal design matrix. In this case, extreme care must be exercised not to read too much into the results. Referring specifically to section 4, table 1, page 3 of the appendix to Ethyl's reply comments and similar regression analysis utilized by Ethyl throughout their fleet, their data analysis is symptomatic of a complete lack of regression understanding. From this table, for instance, the conclusion is made that both Mn and surface area improves conversion efficiency. It may be true, but this conclusion cannot be reached through Ethyl's regression analysis. Because

the coefficients in the regression are aliased with other effects (non-excludable chemical and physical effects). When the $[Z'Z]^{-1}$ comes from a non-orthogonal design, invariably coefficients intended to describe similar effects are combinations of other effects. Significance testing is therefore precluded, as in the presentation by Ethyl. As an example of a simple case taken from a statistical text by Box and Draper, Empirical Model Building one can see mathematically:

$$A = (Z_1'Z_1)^{-1}Z_1'Z_2 = \begin{vmatrix} 5 & 5 \\ 5 & 51 \end{vmatrix}^{-1} \begin{vmatrix} 51 \\ 89 \end{vmatrix}$$

$$= \frac{1}{230} \begin{vmatrix} 51 & -5 \\ -5 & 5 \end{vmatrix} \begin{vmatrix} 51 \\ 89 \end{vmatrix}$$

$$= \frac{1}{230} \begin{vmatrix} 2156 \\ 190 \end{vmatrix}$$

$$= \begin{vmatrix} 9.374 \\ 0.826 \end{vmatrix}$$

$$E(b_0) = \beta_0 + 9.374\beta_{11}$$

$$E(b_1) = \beta_1 + 0.826\beta_{11}$$

We see that $b_0 = 66.777$ is not an unbiased estimate of β_0 in the true quadratic model but is instead an estimate of $\beta_0 + 9.374\beta_{11}$. Similarly, $b_1 = 2.063$ is an estimate of $\beta + 0.826\beta_{11}$, rather than of β_1.

(2) "He (Heinen) states the Mn_3O_4 does not cause macro or micro plugging which affects catalytic reaction at the Canadian concentration of 1/16 gram Manganese per gallon" (Attachment 5). Referring specifically to the three questions he raises on page 4 - section 5:

- "Does the Mn_3O_4 continue to grow with exhaust flow or do they reach an equilibrium level?" Mn_3O_4 continues to grow and at a much higher rate than shown in the graphs. Mr. Heinen could not with his biased curve fitting technique conclude that it does not. Furthermore, nearly all the graphs Mr. Heinen uses (1 to 21) have been biased to a small scope. In fact, most of the graphs are simply wrong when compared to a regression fit, so the graphs not only are in error but very misleading. As an example figure 4 show a Minitab analysis of the same data which indicate the incorrectness of his assumptions. The data scatter shown in graphs 14 to 21 indicate that covariances have either been overlooked in the relationship or that in fact MMT is very unpredictable in its potential reactions on the catalyst (or simply he plotted the wrong relationships to begin with). If as Ethyl states that their fleet is customer reflective, it is obvious that this scatter will permeate to the general public fleet.

- "Are the deposits stable on the surface?" The deposits are stable on the surface but whether a possible reaction has or occurs can only be shown with a more in-depth metallurgical analysis. Surface morphological examination using the SEM show the surface to be a porous, fluffy-like structure. However, in the optical and SEM examination of the cross-section of catalyst, the Mn_3O_4 layer becomes thick and dense and is not as porous appearing as was indicated by the surface morphological examination. Electron microprobe scans do indicate a penetration of Mn into the washcoat (refer to initial submission). If a metallurgical reaction has taken place between the Al and Mn to form an Al-Mn rich intermetallic, it is unknown and further work will have to be done to resolve that issue.

- "Are the deposits truly porous or do they restrict the catalyst effectiveness?" The deposit are not porous. Someone without obvious SEM expertise might conclude from the surface morphology that the deposits are porous but, when viewed cross-sectionally, the microstructure shows a dense nonporous structure. It is evident that this dense nonporous deposits restrict the catalyst effectiveness, due to mass transfer limitation. The mass transfer limitation effect has been shown vividly and conclusively not only in Ford's data, but also in earlier publications.

Mr. Heinen also on page 11 - section 5 refers to the oxygen sensors tested in the last series of Ford analysis. The abnormal behavior exhibited by one of the sensors could have been caused by the buildup of Mn_3O_4 on the surface of the sensor, Figure 5 shows a micrograph of a layer of oxide approximately 5-10 microns thick. This layer would decrease the response time of the sensor. In addition, as far as we know the oxygen sensors from Ethyl's "real world" fleet have not been examined to determine their alleged excellent performance. He further speculates that maybe the specification limits for the sensors may be too broad. This may be true. If the emission standards are to be met for LEV and ULEV, this specification will have to be tightened and with it the effect of Mn_3O_4 on the oxygen sensor becomes more apparent and critical. Quoting Mr. Heinen's speculations on the future of emission standards (page 13, section 5) "Consulting Nostradamus may be more productive", one would not want to put much validity into any of his comments in view of the recent enacted CARB emission standards and those Federal 1993 clean air standards.

(3) **(Contractor) Systems Application:**

(Reference to 50K and 75K conversion efficiency tests for all pollutant tables.)

(a) The efficiency data values are point estimates and also suffer from lack of statistical confidence. These could have been attached. The real problem is that not enough data were obtained to detect differences in the efficiencies. All we can say is that because of the high test variability, any real differences would not be detected, although they probably existed.

(b) It is assumed that when Systems say "Sig.Level", what they really mean is "p-value" for all the tables.

There is not enough clarification as to techniques used in the non-parametrics. If tests were made at the 95% confidence level, then:

[i] If these are 2-sided tests, for columns noted (b), values larger than 2.5% should be ignored.

[ii] If these are 1-sided tests, values larger than 5.0% should be ignored.

Assuming [i], even with the extremely high test variability, none of the non-par tests indicated <u>any</u> beneficial effect of MMT, including analysis with weighted averages!

On a t-test basis (equivalent to the sign test, assuming normality which is highly doubtful), only six of potentially 40 model conditions showed any beneficial effects of MMT; 34 showed no beneficial effects for MMT, some indicating an averse affect of MMT.

Only two of six of the weighted average pollutant-mileage combinations indicated a benefit for MMT.

(4) Ethyl failed to design and carry out an experiment that would detect specific size differences in the emission values if they existed. The techniques are well known. The approach would have required some degree of replication from point to point.

To have utilized sample sizing (or replication), an estimate of the correct variance would have had to have been used. The w/n day variance (or variability over the two or three tests/vehicle points) would have been an incorrect statistic. An estimate of long-term variability would have been needed. This value is probably available and is an estimate of the variation based on long-term testing (nearly a plot error) on a baseline vehicle or set of vehicles.

On an ANOVA basis, the true (test) error structure would have generally appeared as follows:

Source	EVMS
Additive (MMT/clear), A	$\sigma_{e_2}^2 + a\sigma_{LE_2}^2 + d\sigma_{A_2}^2$
Distance (miles), D	$\sigma_{e_2}^2 + a\sigma_{LE_2}^2 + c\sigma_D^2$
AD	$\sigma_{e_2}^2 + a\sigma_{LE_2}^2 + b\sigma_{AD}^2$
Error, (long term) LE	$\sigma_{e_2}^2 + a\sigma_{LE}^2$
w/n error, T	σ_e^2

To determine significance, the MS_A would be tested (F-test) against MS_{LE}. This was not done, as well as could be determined by the Ethyl report.

Estimates of MS_{LE} would have been the appropriate variability to use in determining the number of replicates needed at each mileage point for the specific vehicles. It should be pointed out that at best $\sigma_e^2 + a\sigma_{LE}^2$ would be at least as great as σ_e^2, probably significantly larger.

Catalyst Activity

1.6L 1983 Escort 38,792 miles

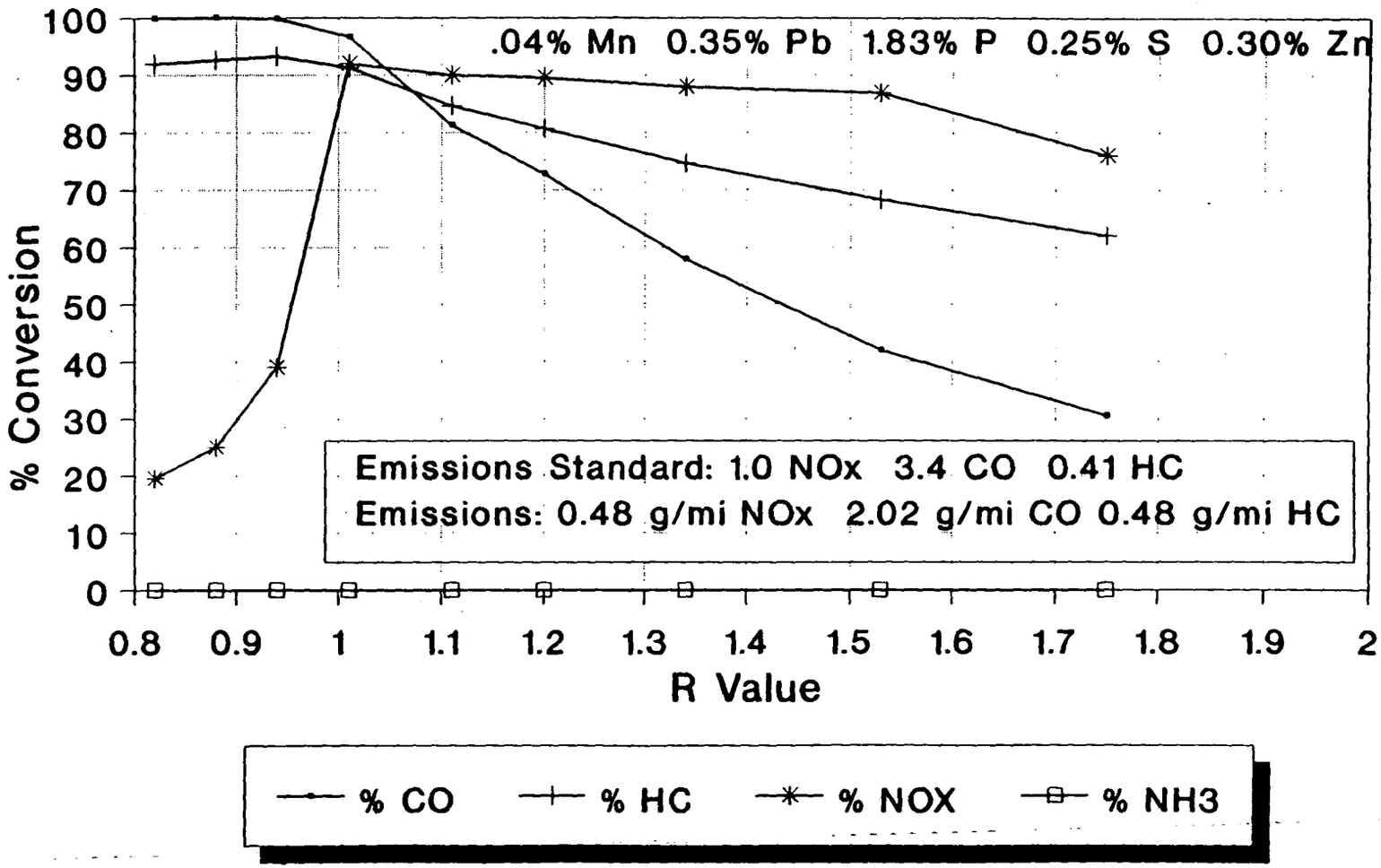


Figure 1

Catalyst Activity

2.3L 1986 Validation Vehicle @120K mile

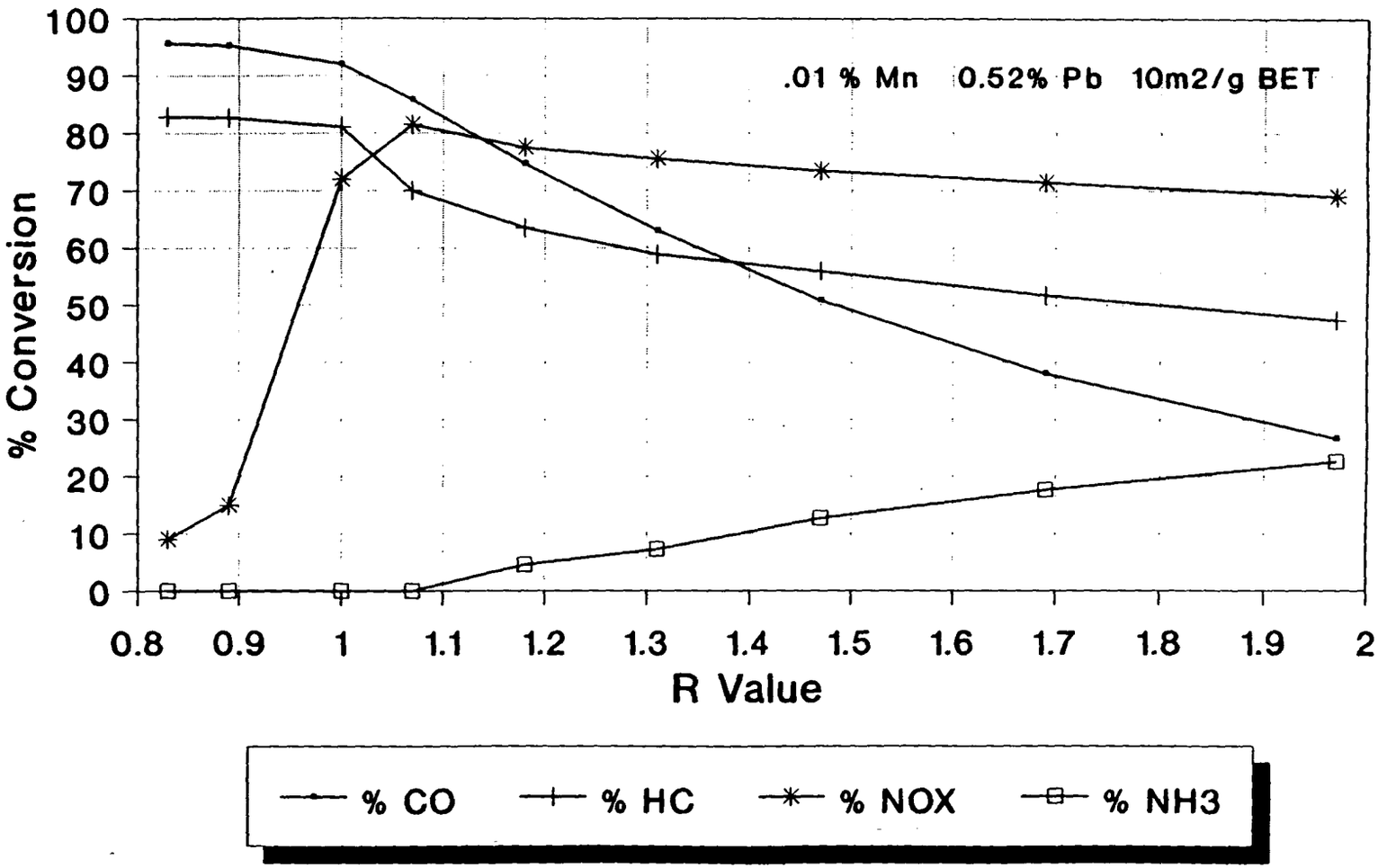
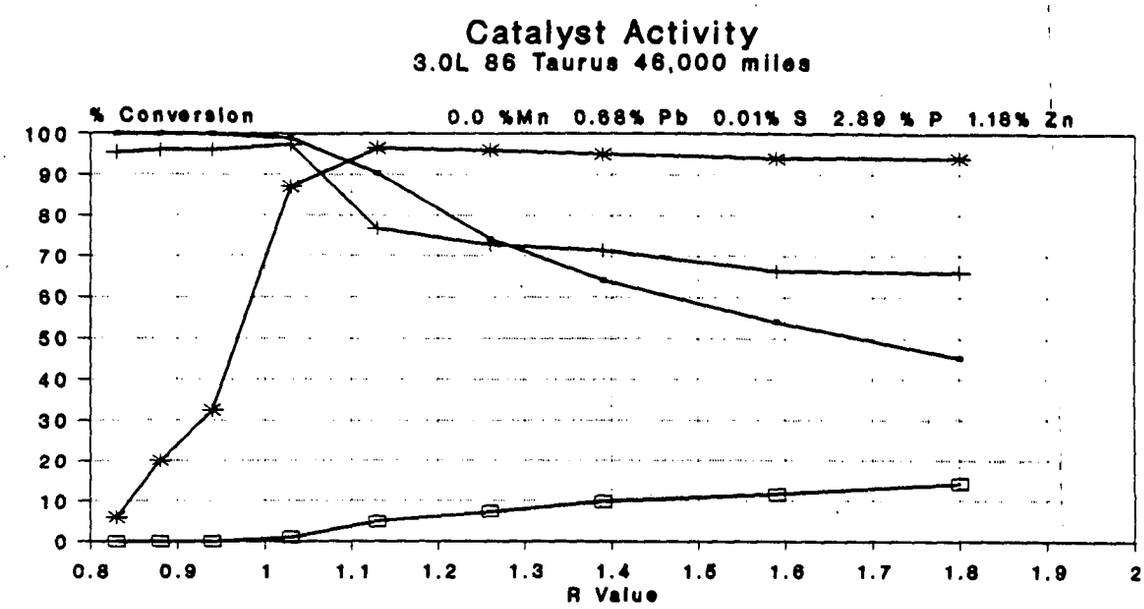


Figure 2



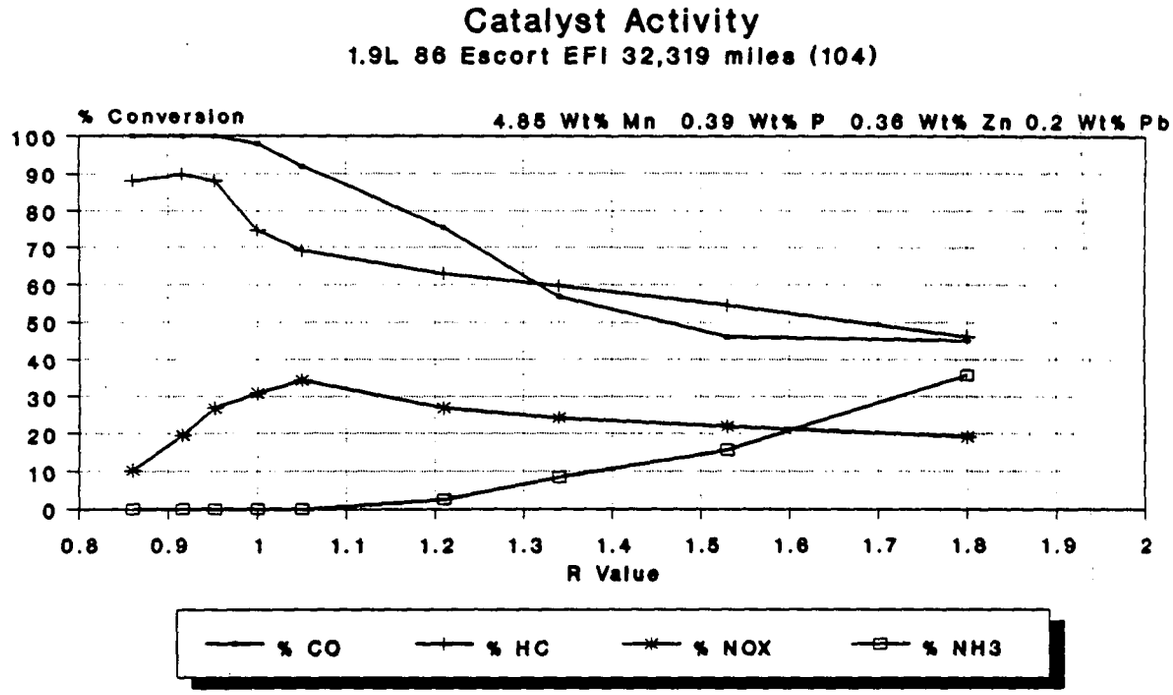
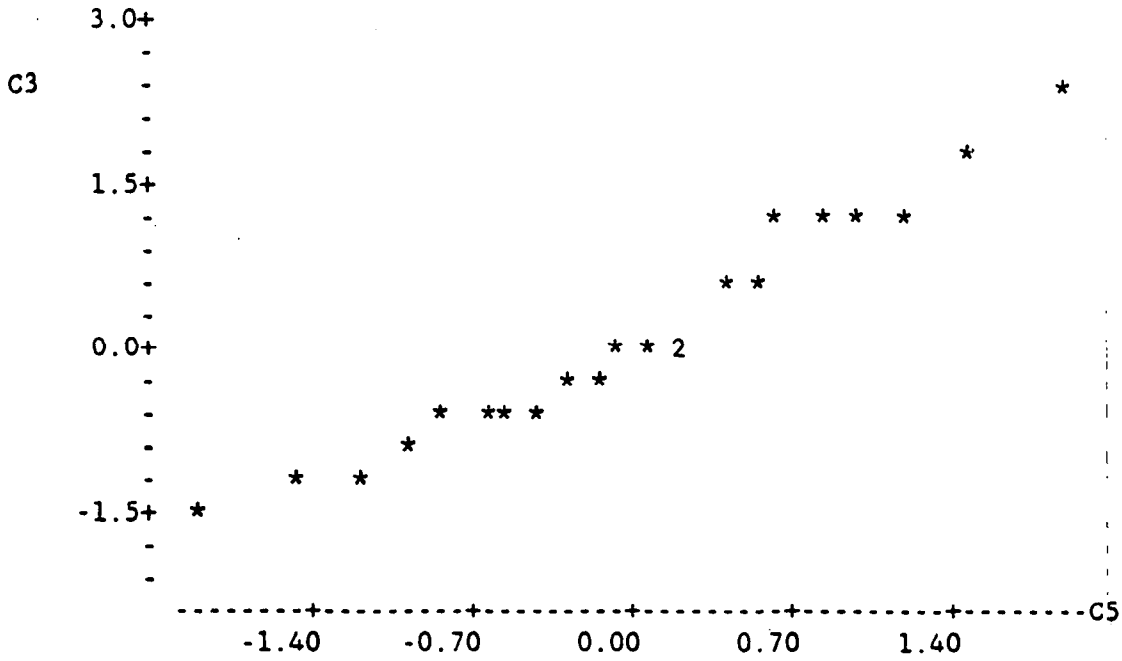
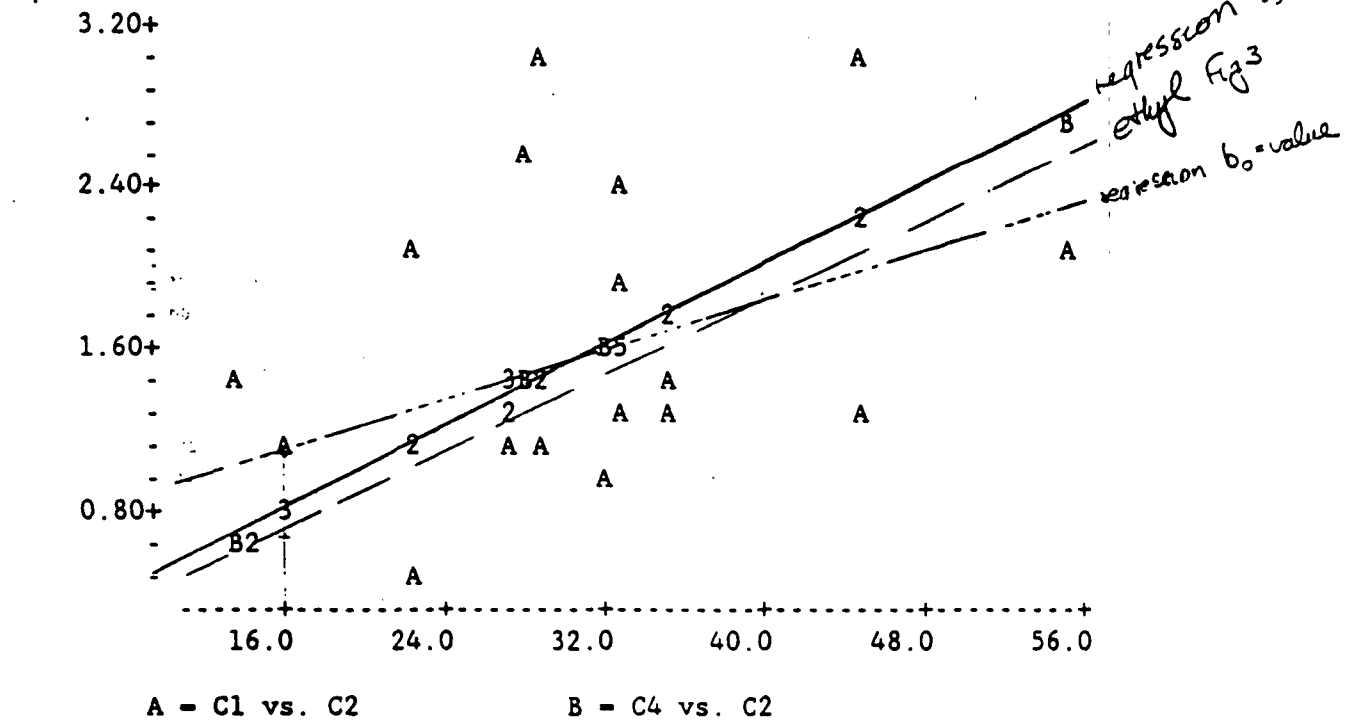


Figure 3

Comparison between Non-MMT Fueled and MMT Fueled Vehicles




```
MTB > mplot c1 c2, c4 c2
```



A = C1 vs. C2 B = C4 vs. C2

```
MTB > noou
```

Figure 4

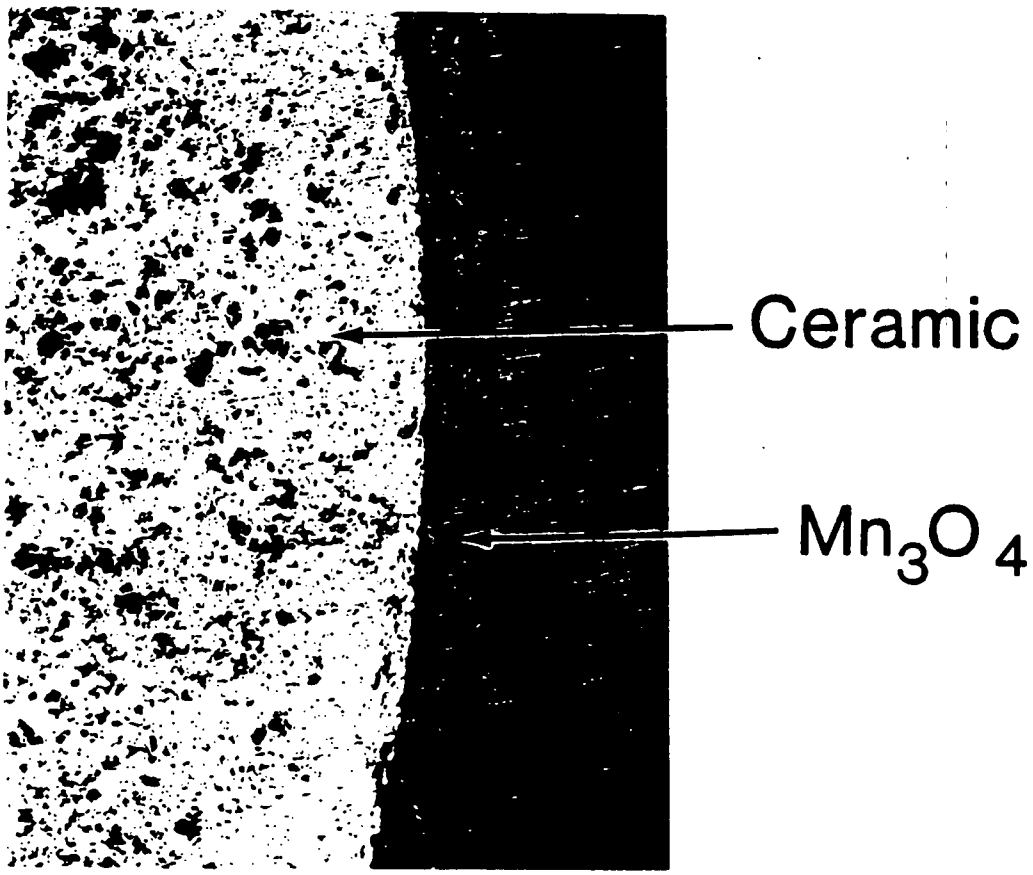


Figure 5

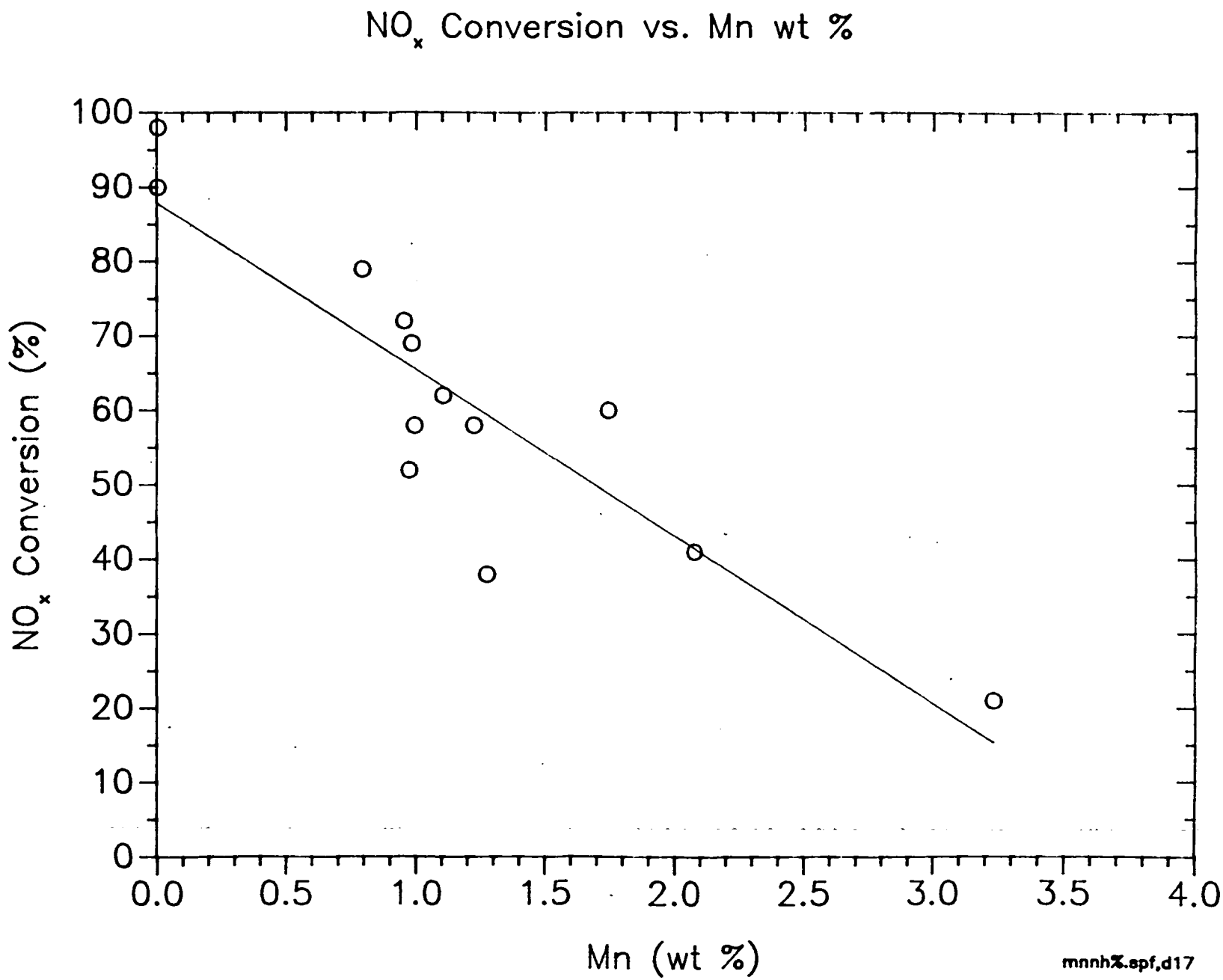

NO$_x$ Conversion vs. Mn wt %
NO$_x$ Conversion (%)
100
90
80
70
60
50
40
30
20
10
0
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Mn (wt %)
mnnh%.spf,d17

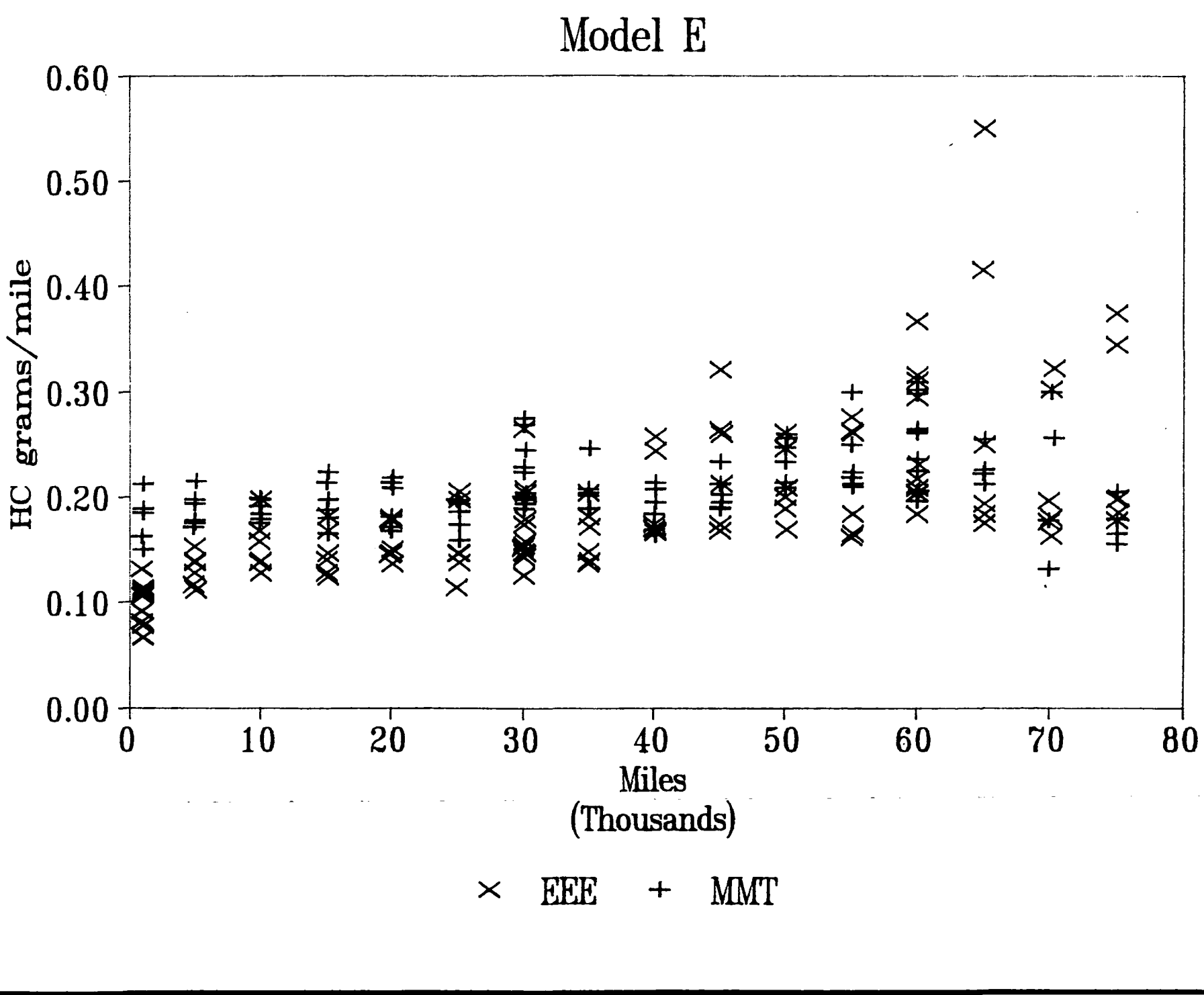
Figure 6

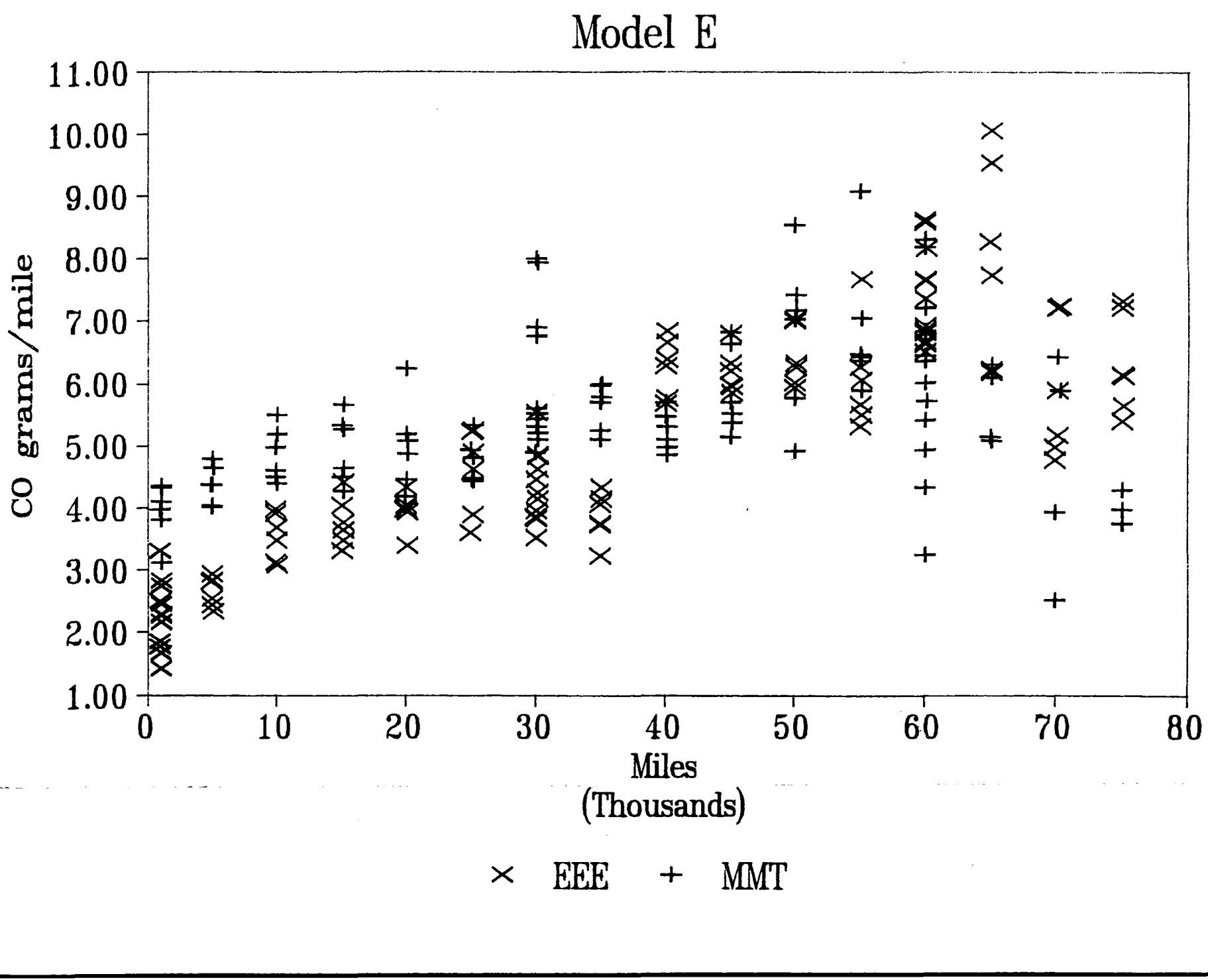
NH3 Formation vs. Mn wt %
50
40
30
20
10
0
NH3 (%)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Mn (wt %)
mnnh3.spf,d17

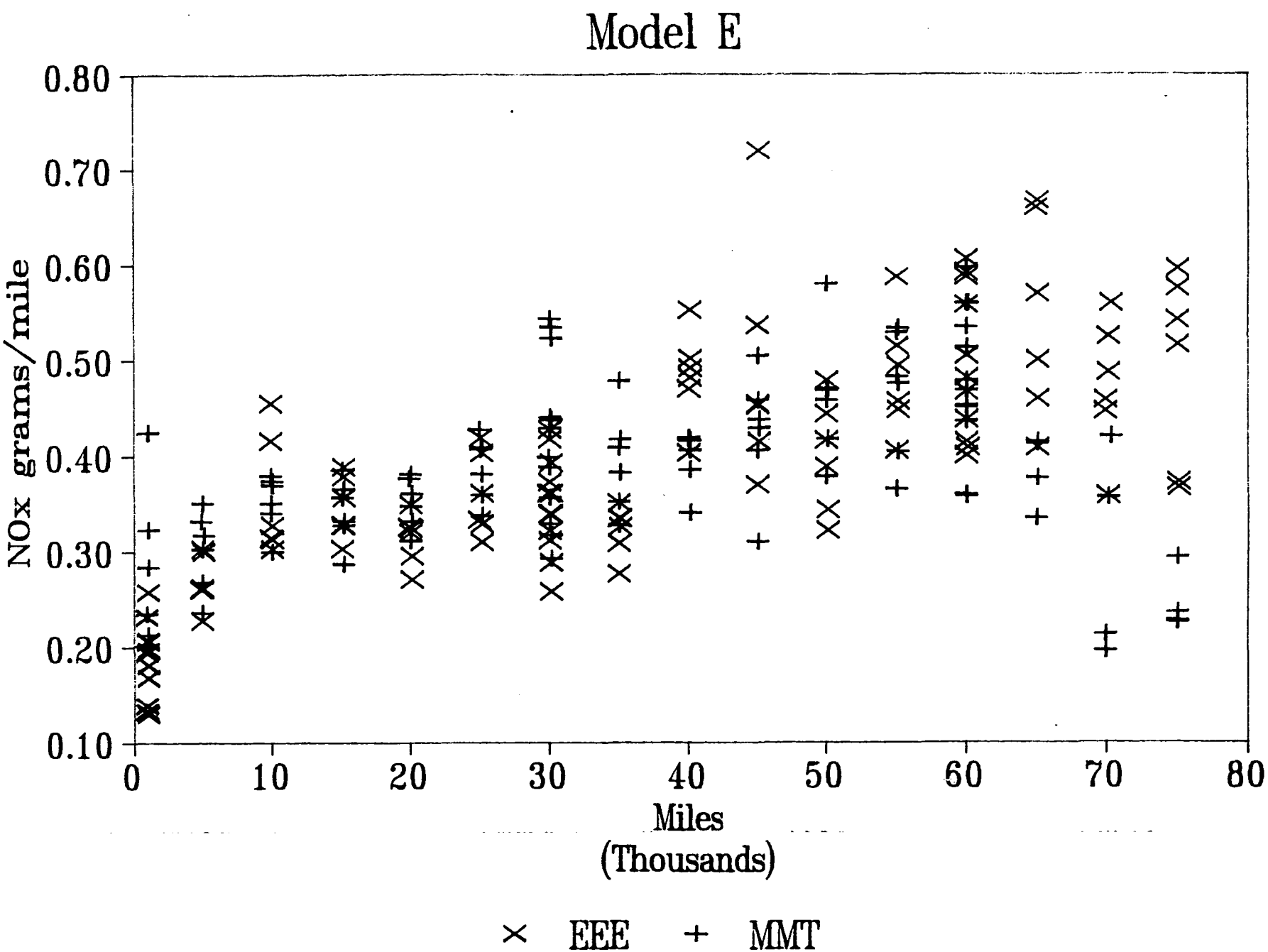
Figure 7

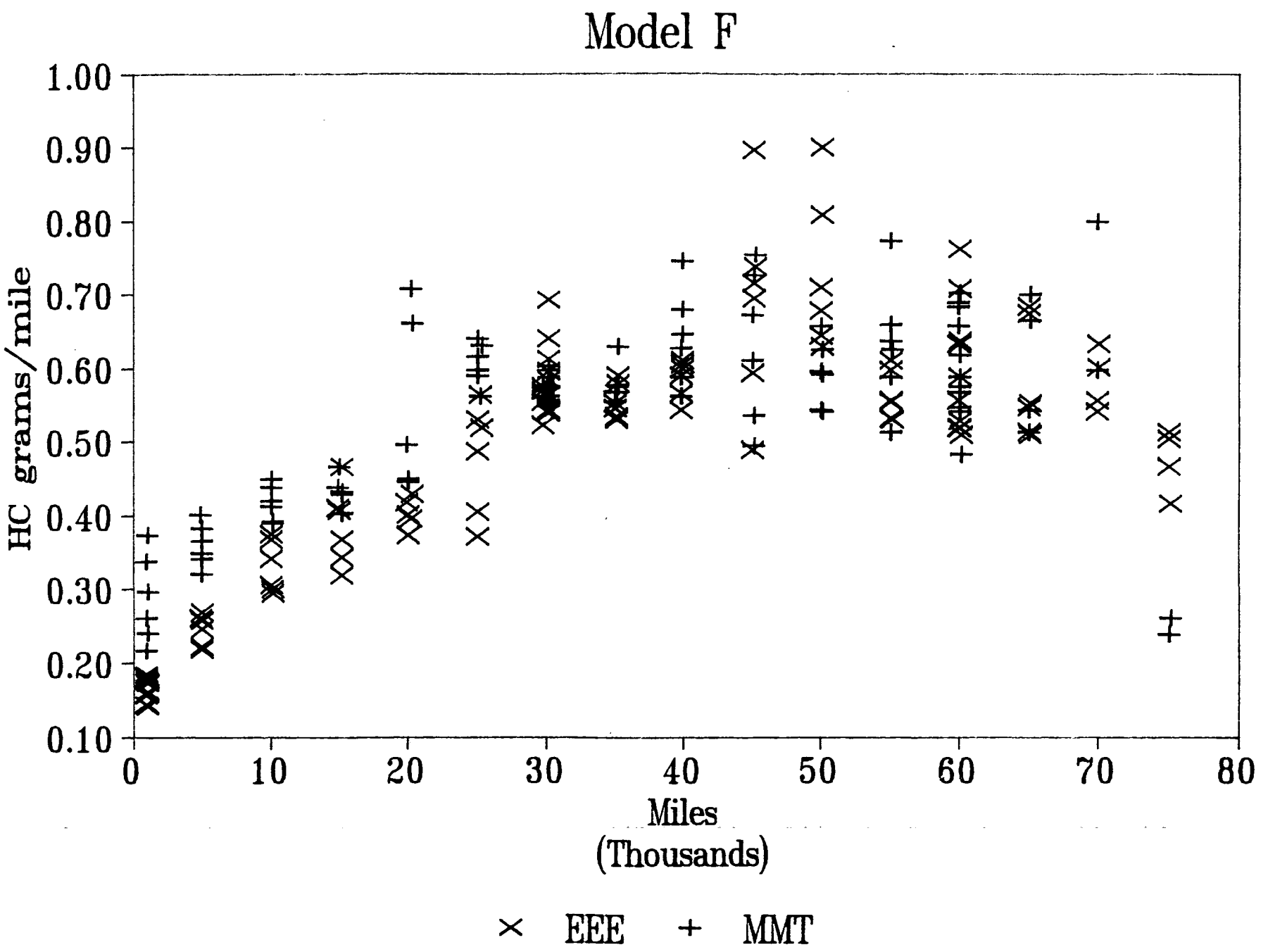
ATTACHMENT 2

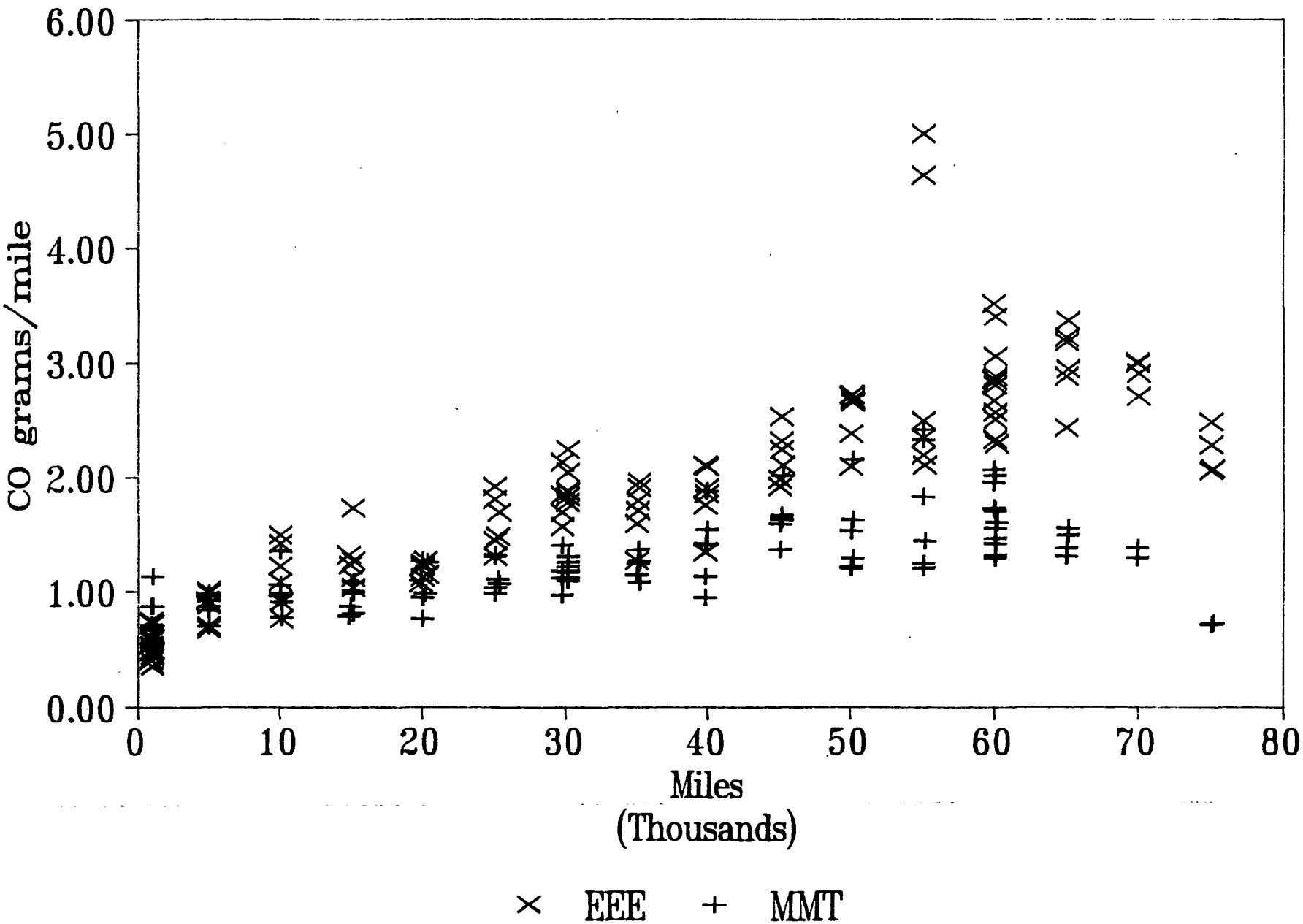
Note: The following charts, which demonstrate the high level of variability in the test data, were made from the fleet emission data provided by Ethyl.

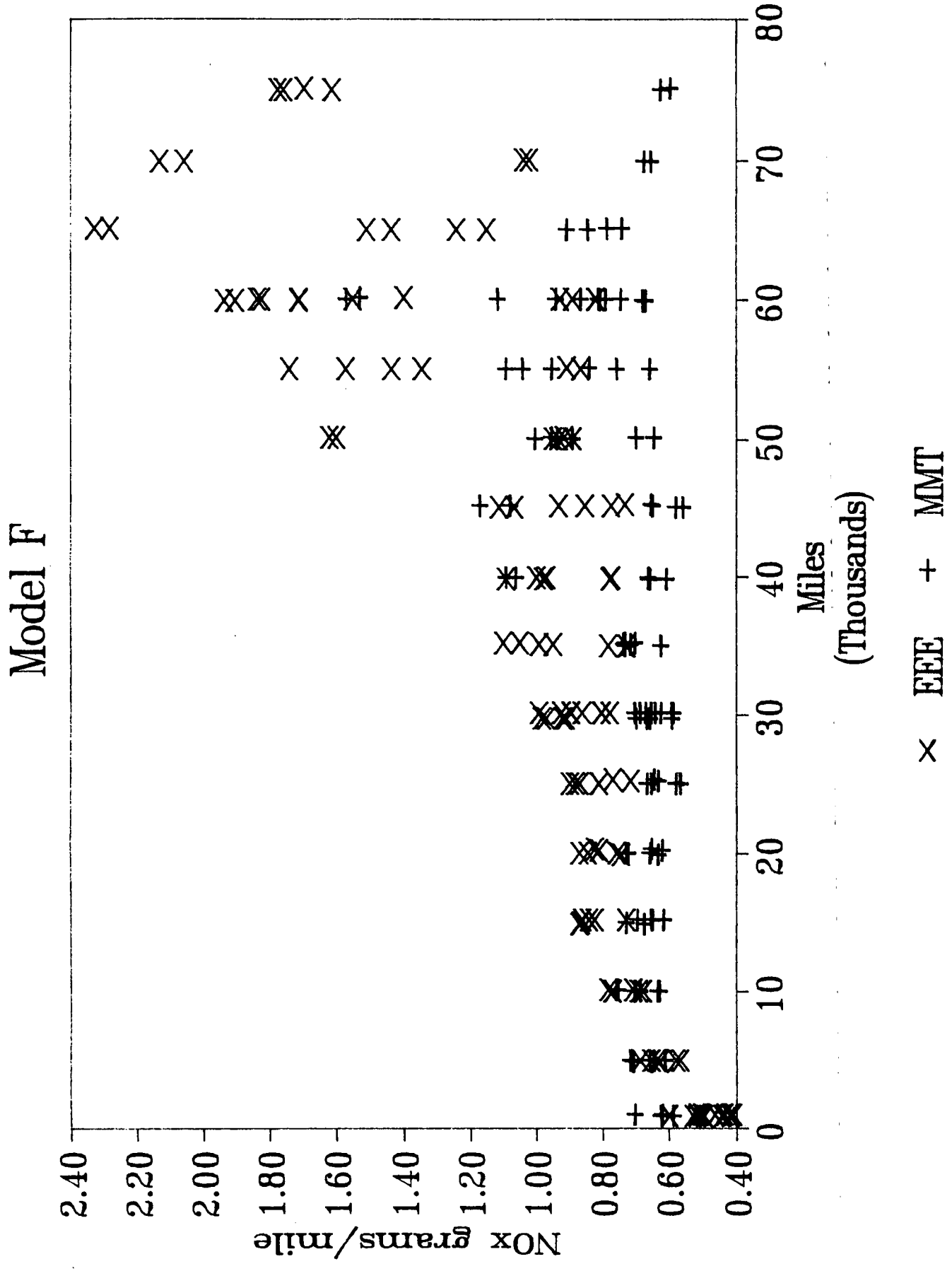

Model E
HC grams/mile
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
× EEE + MMT

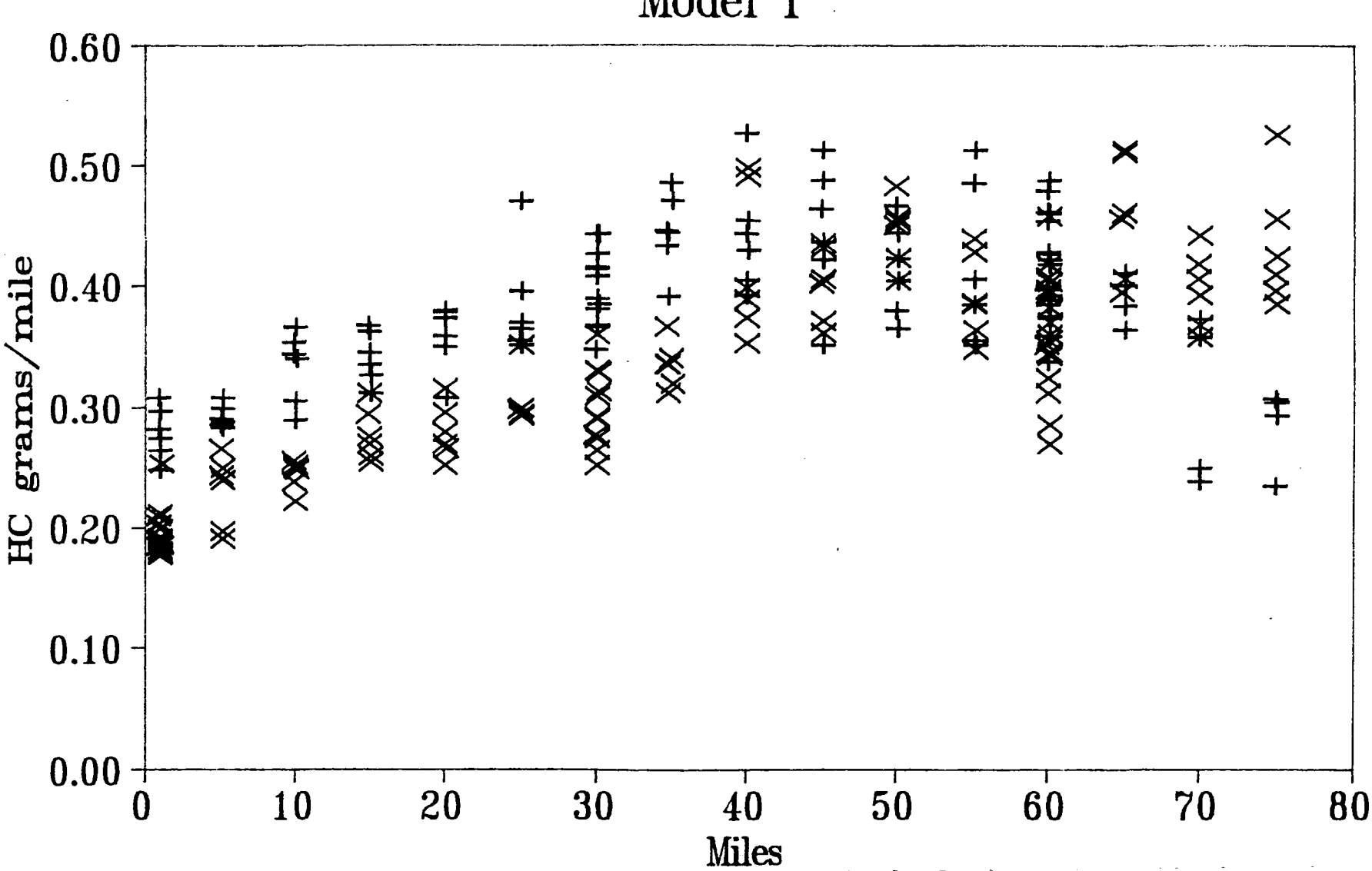

Model E
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
CO grams/mile
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
EEE
MMT

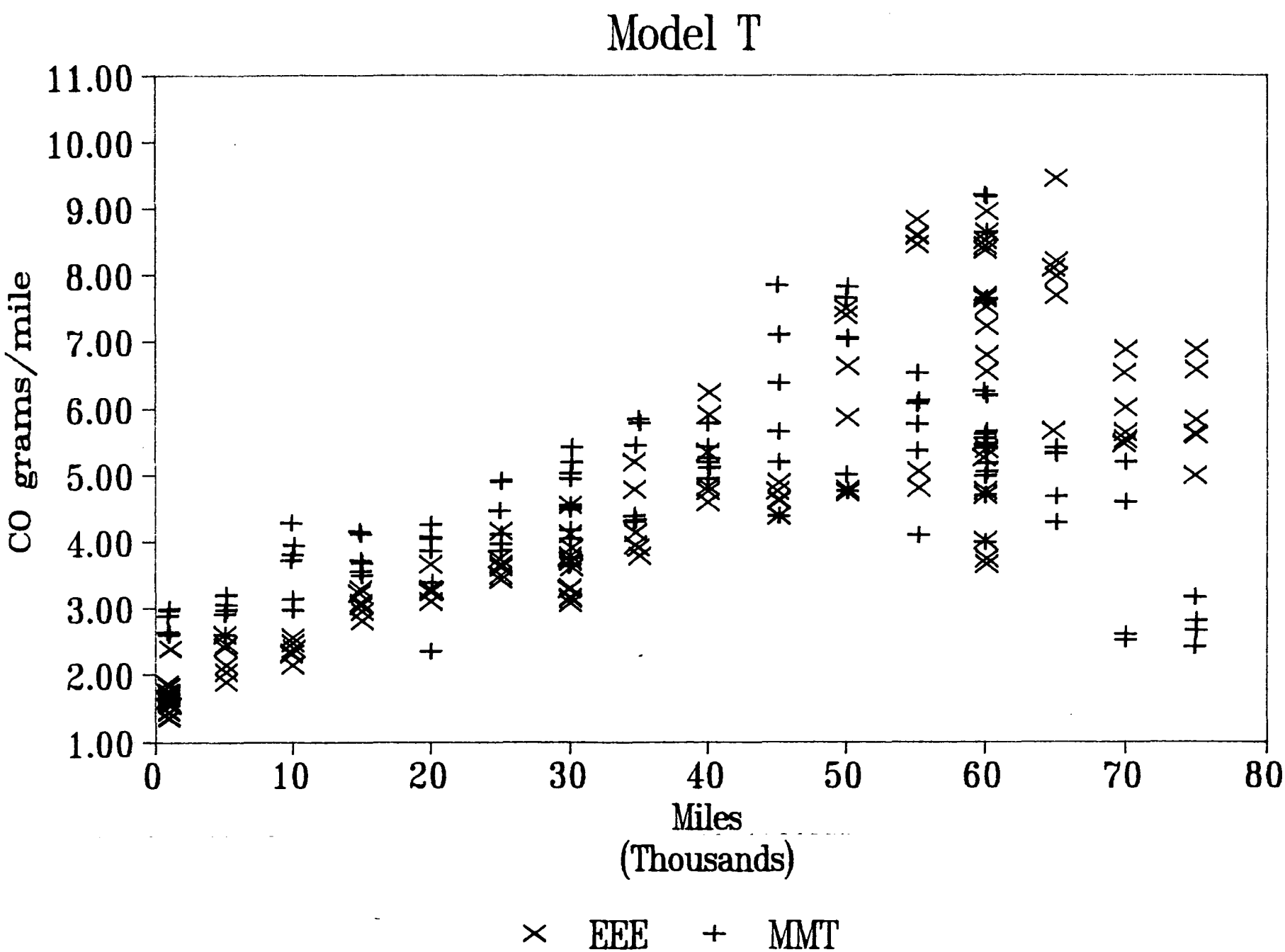

Model E
NOx grams/mile
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
× EEE + MMT

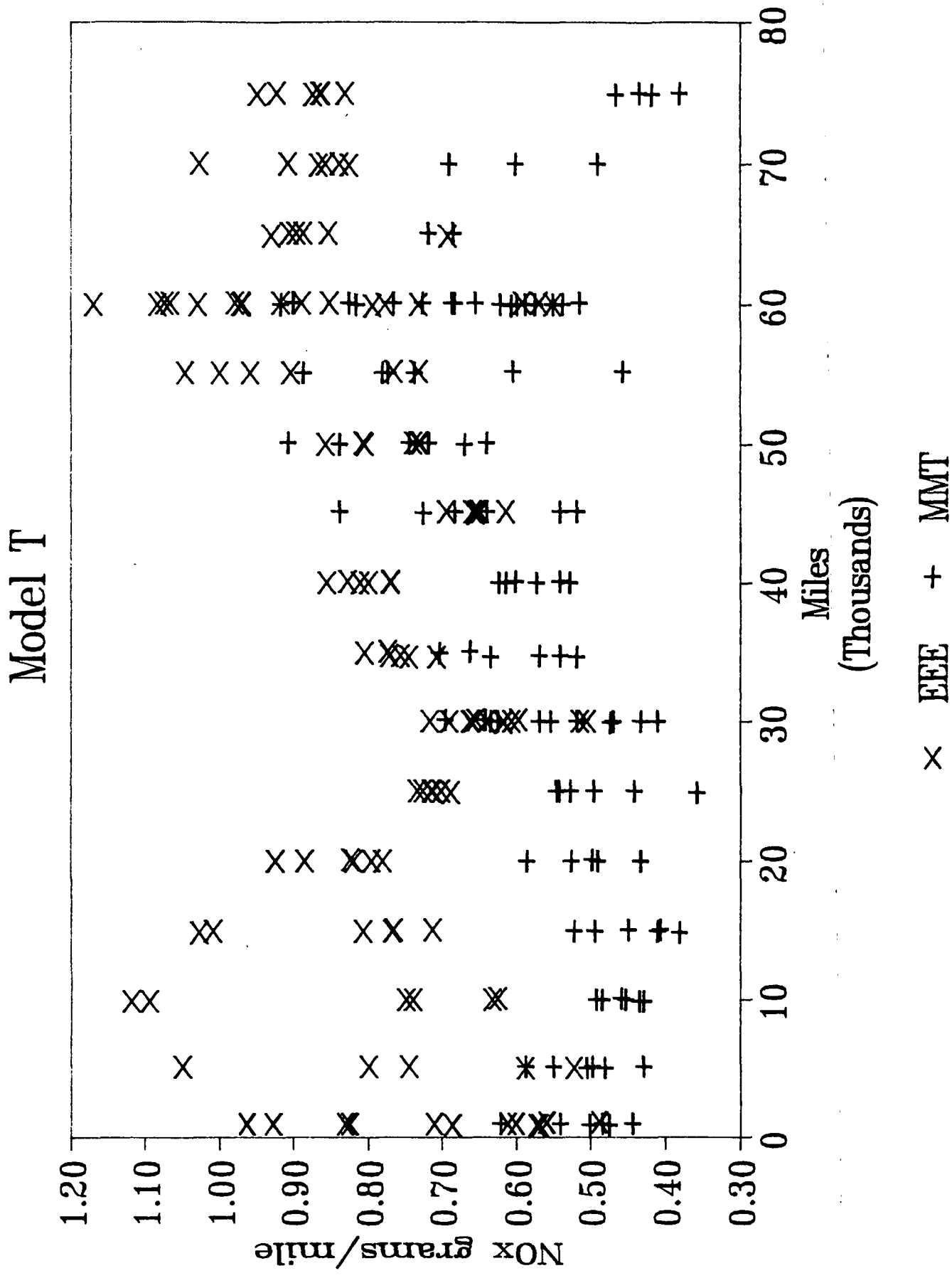

Model F
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
HC grams/mile
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
× EEE + MMT


Model F
6.00
5.00
4.00
3.00
2.00
1.00
0.00
CO grams/mile
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
× EEE + MMT


Model F
NOx grams/mile
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
X EEE + MMT


Model T
HC grams/mile
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
EEE
MMT


Model T
11.00
10.00
9.00
8.00
7.00
6.00
5.00
4.00
3.00
2.00
1.00
CO grams/mile
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
× EEE + MMT


Model T
NOx grams/mile
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0
10
20
30
40
50
60
70
80
Miles
(Thousands)
X EEE + MMT

ATTACHMENT 3

Helen O. Petrauskas
Vice President
Environmental and Safety Engineering

Ford Motor Company
The American Road
P. O. Box 1899
Dearborn, Michigan 48121-1899

July 3, 1990

Dear Mr. Ter Haar:

Thank you for taking the time to meet with us on June 5, 1990 to share the results of your MMT test program. Your program provides some very valuable information on the effects of MMT on exhaust emissions. As with any research program, however, new questions were raised. As a result, we agreed in that meeting to share with you our thoughts as to what further work could be done in order to attempt to resolve these open issues.

We strongly believe that a key factor in the determination of the effects of MMT is the post-mortem analyses of the components of the emission control system, in particular the catalyst and oxygen sensor, from the test vehicles which have been operated on fuel containing MMT. These analyses would include the following tests which should be performed on the catalytic converters and oxygen sensors after they have been removed and photographed:

- Analysis by x-ray fluorescence
- BET surface measurements
- Microprobe for contaminant depth profile
- Optical and scanning electron microscopic examination of the washcoat conditions
- Determination of catalytic converter efficiency by steady-state and light-off curves
- Determination of oxygen sensor efficiency by sensor response delay

We would be pleased to assist in any way we can should you decide to proceed with this testing.

Additionally, in order to determine the effects of MMT on actual, in-use vehicles, similar post-mortem tests should be conducted on catalytic converters removed at random from Canadian vehicles which have been exposed to MMT. The analysis of catalytic converter attributes and performance (i.e., BET and efficiency) should sufficiently demonstrate the actual real life, long-term effects of MMT on in-use catalytic converters. Although we realize that the concentration of MMT in the Canadian gasoline is twice that which you are currently proposing, we still believe that valuable information concerning the effects of MMT on emission control systems may be gathered from these tests.

The vehicles selected for these physical and chemical characterization tests should represent a statistically significant cross-section of all Canadian Provinces. The vehicles should have documented maintenance, driving, and fueling records. The analysis should be performed not only on the catalytic converters, but also on other emission components (i.e., oxygen sensors and fuel injectors) from each of the vehicles selected for testing.

Finally, we are concerned about the use of Howell EEE fuel for mileage accumulation in the baseline vehicles in your program. This fuel, which lacks detergents, is not representative of commercially-available, real-world gasoline. Lack of fuel detergents could cause an increase in the intake fuel system deposits and thereby result in an unrepresentatively high baseline as a reference point. These intake system deposits may also lead to some "hot spots" which could affect engine out emissions.

I hope that you will find these recommendations helpful. If you have any further questions, please contact Mr. Kelly M. Brown at 313/322-0033 or Mr. David L. Kulp at 313/323-8937.

Sincerely,

Kelly M. Brown for

H. C. Petrauskas

Mr. Gary L. Ter Haar
Vice President
Health and Environment Department
Ethyl Corporation
451 Florida Street
Baton Rouge, Louisiana 70801